



# Influence of plasma treatment on electrochemical activity of Ni (o)-based catalyst for hydrogen production by hydrolysis of NaBH<sub>4</sub>

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## HIGHLIGHTS

- Catalytic properties of Ni(0) with plasma were investigated.
- Produced Ni(0) catalyst applied to hydrogen generation from the hydrolysis of NaBH<sub>4</sub>.
- Hydrolysis with Ni(0) catalyst by using plasma completed in 35 min.
- Ni(0) catalyst produced in known method was completed in 80 min.
- Ni<sup>2+</sup> species of the catalyst sample is almost completely reduced to Ni(0).

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## ABSTRACT

In this study, the hydrogen generation from the hydrolysis of NaBH<sub>4</sub> with Ni (o) catalyst prepared in the presence of plasma is investigated. The catalytic properties of nickel catalyst prepared in the presence of plasma are investigated based on NaBH<sub>4</sub> concentration, NaOH concentration, temperature, plasma applying time and plasma applying voltage. The results indicated that nickel catalyst reduced with plasma was completed in only 35 min, while the nickel catalyst produced in known method is completed in 80 min. Characteristics of this nickel-based catalyst are carried out by using XRD, BET, SEM and XPS. The activation energy for zero-order is found to be 51.35 kJ mol<sup>-1</sup>.

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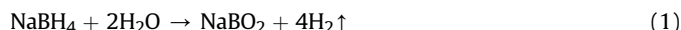
## 1. Introduction

A large portion of the world energy demand is meeting by the fossil fuels. However, it is estimated that, the fossil fuel production worldwide will continue to rise for the next few decades, and then will start to decrease because of rising global energy and fossil fuel consumptions [1].

Energy and environmental concerns that affect our current energy system focused on fuel cells attracting more and more attention as clean and efficient power generation devices. Hydrogen based energy technologies are a major topic of international importance for energy supply and environmental protection [2,3]. Hydrogen fuel cells attract more attention because hydrogen is supposed to be pollution free. However, its production and use still

require energy-consuming and costly processes, and the need for new infrastructure.

Schlesinger et al. [4] made a detailed study on the hydrolysis reaction of NaBH<sub>4</sub> for hydrogen generation. Hydrogen is generated from NaBH<sub>4</sub> by following hydrolysis reaction:



At room temperatures, only a small percentage of the theoretical amount of hydrogen is liberated by hydrolysis reaction of NaBH<sub>4</sub> and H<sub>2</sub>O [5,6]. However, the efficiency of hydrogen production can be significantly accelerated by use of catalyst like metals and their salts during the reaction [7]. Catalytic hydrogen gas generation from NaBH<sub>4</sub> solutions has many advantages such as the NaBH<sub>4</sub> solutions nonflammable, the reaction products environmentally benignable, the rate of hydrogen generation easily controllable, the reaction product NaBO<sub>2</sub> recyclable, hydrogen generatable even at low temperatures.

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Catalysts such as Ru supported catalyst [8–12], cobalt-based catalyst [13–18], Ni-based catalyst [19,20], Cu–Co based catalyst [21], Ni–Co–B [22] etc. have been developed to accelerate the hydrolysis reaction of the  $\text{NaBH}_4$ . All of these catalysts used in hydrolysis of  $\text{NaBH}_4$  act as heterogeneous catalysts [23]. The limited surface area of the heterogeneous catalysts causes to a lower catalytic activity.

In recent years, plasma techniques had attracted considerable attention in the field of preparing effective catalysts [13,20,24–30]. Plasma is an ionized gas that can be generated by a number of methods. It is usually classified as a high temperature (or thermal) plasma and a cold (or non-thermal or nonequilibrium) plasma. Cohn et al. [31,32] show that comparable hydrogen yields could be attained with both kinds of plasma, but at significantly lower energy consumption in the case of non-thermal plasma. Chun et al. stated that plasma not only provides energy to the system but also generates radical and excited species, allowing, initiating and enhancing the chemical reactions. The advantages of plasma relate to the low temperature that will result in less energy consumption and minimum electrode erosion [33]. A major advantage of plasma is its rapid response without induction period that exists in the conventional catalytic reforming processes [34–37].

In this study, the catalytic properties of Ni (o) prepared in the known method and presence of plasma were investigated for hydrogen production from hydrolysis of  $\text{NaBH}_4$ . The plasma treatment enhances the Ni (o) reactivity in hydrolysis of  $\text{NaBH}_4$  to release hydrogen. In the literature, although several data exist on the usage of Ni and Ni–B catalyst for the hydrolysis of  $\text{NaBH}_4$ , there is no published data for the examination of plasma applying Ni (o) catalyst for hydrogen production from the hydrolysis of  $\text{NaBH}_4$ .

## 2. Experimental

$\text{NaBH}_4$  (molecular weight:  $37.83 \text{ g mol}^{-1}$ , assay 98%, Aldrich Chemical Co.) was used for the catalytic properties of Ni (o). The solubility of  $\text{NaBH}_4$  in water at  $25^\circ\text{C}$  is  $55 \text{ g/100 g}$  water, but the solubility of sodium metaborate is  $28 \text{ g/100 g}$  water. In this study, the hydrogen generation from  $\text{NaBH}_4$  hydrolysis with prepared Ni (o) catalyst was tested depending on plasma applying voltages (10–20 kV), plasma applying times (10–20 min),  $\text{NaBH}_4$  (3.2–10%) and NaOH (1.5–10%) solutions, catalyst amount (50–200 mg) and temperature ( $20$ – $60^\circ\text{C}$ ).

### 2.1. Reactor

Apparatus of plasma reactor under argon gas atmosphere is described in Fig. 1. The reactor is a cylindrical Pyrex tube with high voltage copper electrode as the inner metal electrode and aluminum film coated at the outer side of tube as the outer electrode. The dried precipitate sample was put into the reactor and treated by argon plasma for 10 min. Plasma was generated by an alternating current power supply that has a maximum voltage of 20 kV. A digital power meter was inserted to the electric line of the power supply in order to measure the total supplied power to then reactor.

### 2.2. Catalyst preparation

All reagents used in this research were of analytical grade. The Ni (o) catalysts were prepared in following two ways:

- a. Chemical reduction was carried out by adding drop-by-drop  $0.30 \text{ M}$   $\text{NaBH}_4$  solution into a plasma cell including  $0.09 \text{ M}$   $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solution in the presence of argon gas at  $30^\circ\text{C}$ . The produced black precipitate was separated from the solution,

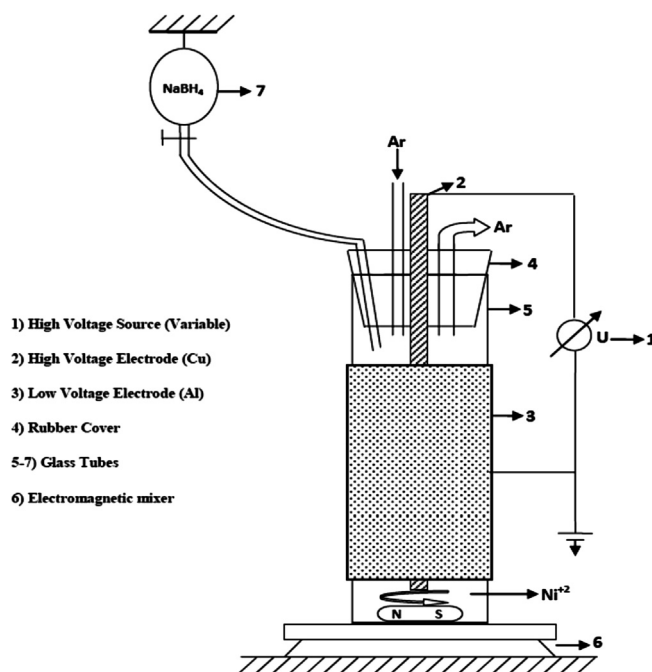


Fig. 1. The system used to prepare Ni (o) catalyst with plasma.

washed by deionized water for three times, and dried in an argon atmosphere system at  $120^\circ\text{C}$ . Then, plasma was applied to the produced Ni (o) catalyst as shown in Fig. 1. The material was stored in airtight plastic container for further use.

- b.  $0.09 \text{ M}$   $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was directly added into  $0.30 \text{ M}$   $\text{NaBH}_4$ . The formed black precipitate was separated from the solution, washed by deionized water for three times, dried in an argon atmosphere system at  $120^\circ\text{C}$ , and kept in airtight plastic container for use.

### 2.3. Catalyst characterization

The surface morphologies of the plasma untreated and plasma treated Ni (o) catalysts were analyzed by means of scanning electron microscopy (SEM) (Zeiss EVO 50 Model). X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition and the oxidation state of the elements on the catalyst surface. The XPS instrument, a VG Escalab 200R spectrometer with an Al  $K\alpha$  X-ray source, was equipped with a pre-treatment chamber with controlled atmosphere and temperature in which the catalyst samples could be treated under various conditions.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer by using Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), over range of  $2\theta = 10$ – $80^\circ$ .

BET surface areas were calculated from the nitrogen adsorption isotherms at  $77 \text{ K}$  by using a Micromeritics ASAP 2000 surface analyser and a value of  $0.164 \text{ nm}^2$ .

### 2.4. Generation of hydrogen

The volume and the rate of hydrogen generated in the presence of catalysts were measured by using a water-displacement method, which was described in detail along with its experimental setup in our previous work [38]. A measured volume of released gas was subsequently converted into yield of produced hydrogen after the total amount of gas had been collected.

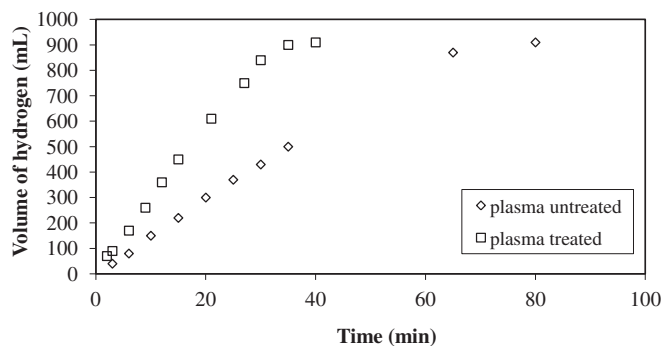


Fig. 2. Hydrogen volume of  $\text{NaBH}_4$  with  $\text{Ni}(0)$  catalyst prepared at plasma and non-plasma media as a function of time.

### 3. Results and discussion

The hydrogen generation from the hydrolysis of  $\text{NaBH}_4$  with  $\text{Ni}(0)$  catalyst prepared in the presence of plasma was investigated. Fig. 2 shows the hydrogen generation volume from  $\text{NaBH}_4$  with  $\text{Ni}(0)$  catalyst produced in the presence of plasma and known method. It can be seen that hydrogen production from hydrolysis reaction of  $\text{NaBH}_4$  with  $\text{Ni}(0)$  catalyst reduced in the presence of plasma is completed in 35 min, while  $\text{Ni}(0)$  produced in the known method let to slow hydrogen release and the hydrolysis is completed in 80 min.

#### 3.1. Catalyst characterization

##### 3.1.1. XPS

Figs. 3a, b and 4a, b show the XPS spectrum of the plasma untreated and plasma treated with  $\text{Ni}(0)$  catalyst under an inert argon atmosphere. As can be seen in Fig. 3a, b, the binding energy of  $\text{Ni } 2p_{3/2}$  in plasma untreated catalyst was 854.82 eV and shifted to 852.14 eV corresponding to the  $\text{Ni } 2p_{3/2}$  level in the plasma treated catalyst  $\text{Ni}(0)$ . As shown in Fig. 3, three peaks were appeared after plasma treatment performed on the catalyst under an inert argon atmosphere. XPS handbook shows that peak 1 at 852.20 eV corresponds to metallic  $\text{Ni } 2p_{3/2}$  peak, and peak 3 at 869.30 eV to

metallic  $\text{Ni } 2p_{1/2}$  peak, peak 2 at 854.60 eV to  $\text{Ni}^{2+} 2p_{3/2}$  peak, respectively [39]. The result revealed that the  $\text{Ni}^{2+}$  species of the catalyst sample is almost completely reduced to  $\text{Ni}(0)$  during the plasma treatment. In addition, the XPS spectra revealed that plasma could apparently improve the number of  $\text{Ni}(0)$  exposed on the surface of catalyst assisted by plasma.

Table 1 summarizes the binding energies of  $\text{Ni } 2p$ ,  $\text{C } 1s$  and  $\text{O } 1s$  levels. Fig. 4a and b displays  $\text{Ni } 2p$ ,  $\text{C } 1s$  and  $\text{O } 1s$ , respectively, core-level spectra of a representative catalyst sample. Still, carbon and oxygen were dominant species on the surface of  $\text{Ni}(0)$  catalyst, whereas the  $\text{Ni } 2p$  concentration value in plasma treated catalyst comparing to plasma untreated catalyst was increased to 20.28% from 15.34%. In addition,  $\text{C } 1s$  and  $\text{O } 1s$  concentration values were decreased (Table 1).

##### 3.1.2. XRD

XRD measurements for two catalysts before and after plasma treatment are shown in Fig. 5. It can be seen that the XRD spectra after plasma treatment are nearly same as before plasma treatment. No apparent change was observed from XRD results. The reason probably is that during the plasma treatment could not result in the crystal change of the catalyst.

##### 3.1.3. BET surface area

The plasma treated catalyst exhibited significantly higher than surface area ( $23.11 \text{ m}^2 \text{ g}^{-1}$ ) compared to plasma untreated catalyst ( $0.0063 \text{ m}^2 \text{ g}^{-1}$ ). The reason probably is that due to the  $\text{Ni}$  catalyst prepared with the plasma method can effectively resist these metal aggregations to possess a high metal dispersion. Therefore, a higher specific surface area was obtained from the plasma activation, which was benefit for the good performance of the novel catalyst.

This phenomenon is consistent with study of Zou et al. [40].

##### 3.1.4. SEM

The surfaces morphologies of plasma treated and untreated the  $\text{Ni}(0)$  catalysts are shown in Fig. 6. As seen by that, surface morphology of plasma treated and untreated  $\text{Ni}(0)$  catalysts is flaky particles that resulting products agglomerate with varying sizes. This kind of morphology might be helpful to enhance the active surface area of the  $\text{Ni}(0)$  catalysts. From Fig. 6(b), it is also found

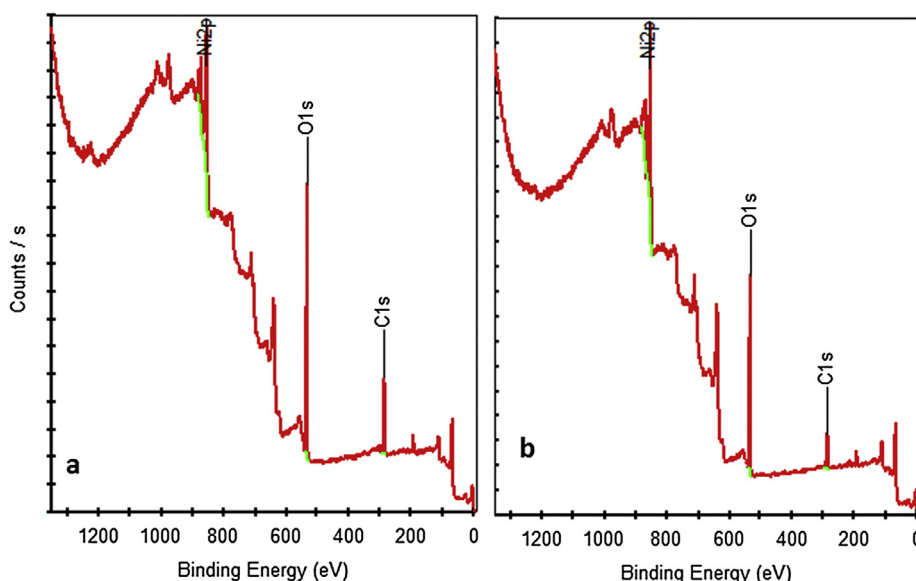


Fig. 3. The comparison of XPS spectra of  $\text{Ni } 2p$  before (a) and after (b) plasma treatment.

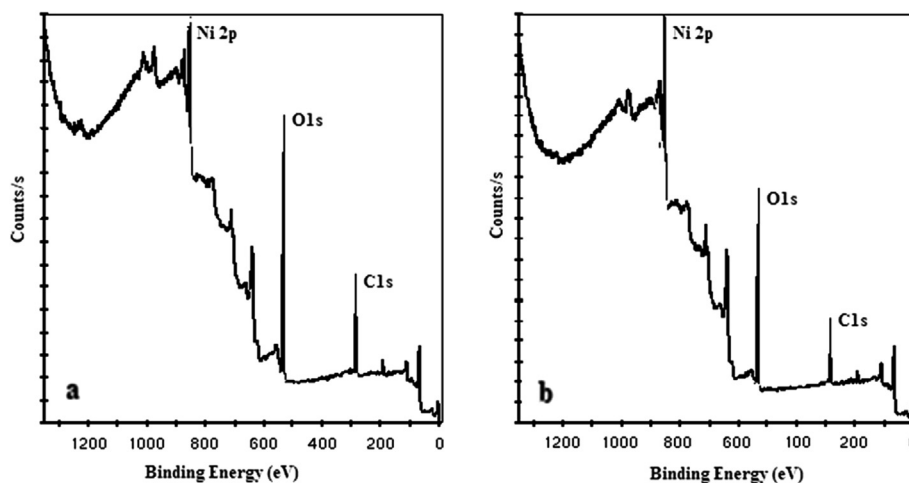


Fig. 4. The binding energies of Ni 2p, C 1s and O 1s levels before (a) and after (b) plasma treatment.

that the surface of Ni (0) catalyst became rough and irregular aggregates after Ni (0) catalyst treated plasma under argon atmosphere.

### 3.2. Effect plasma treatment time

In order to minimize the application time effect of plasma on the activity of Ni (0) catalyst at the reaction reduction step, three different treatment time (10–15–20 min) was applied. Then, Ni (0) catalyst obtained with different reduction time in the presence of plasma was used in the hydrolysis of  $\text{NaBH}_4$  for hydrogen generation. As shown in Fig. 7, the hydrogen generation rate is dependent on the duration of plasma treatment. When the three different applying plasma time effects were compared, it was observed that the hydrogen production rate was very much enhanced by the use of 10 min plasma applying time. It is expected that longer plasma treatment will increase the reduction efficiency. However, it appears that longer plasma treatment on the Ni (0) catalyst was decreased the hydrolysis of  $\text{NaBH}_4$  for hydrogen generation. This phenomenon may occur due to the destruction of micropores because of excessive treatment depressed the specific surface area of the sample [41].

### 3.3. Effect of plasma treatment voltage

Supplied voltage from an electrical generator to the reactor is one of the most important parameters. To investigate the effect of plasma applying voltage on activity of Ni (0) catalyst, the input power was experimentally varied in the range of 10–20 kV, while electrode gap distance and reactor thickness between the reactor glass walls were kept constant. Fig. 8 shows the influence of input plasma voltage on activity of Ni (0) catalyst. As shown in Fig. 8, the plasma treatment voltage of 20 kV at the hydrolysis reaction of Ni (0) catalyst has been observed as the most effective plasma treatment voltage. Increasing the applied voltage to increase the

density of active species could be a way of activating the surface property of the catalyst because of an increase of voltage produced more energy to activate molecules to higher energy levels [42]. The energy supplied in the plasma reactor is used to activate the molecules to a higher energy level or to produce no neutral species, such as electrons and ions. These species have enough capacity to break the chemical bond of catalysts.

### 3.4. Effect of catalyst amount

To examine the effects of Ni (0) catalyst amount, the hydrogen generation yield was measured by hydrolysis of 3.2 wt%  $\text{NaBH}_4 + 10\%$  NaOH solution using Ni (0) catalyst (50, 100, 150 and 200 mg) prepared with plasma at 30 °C. As observed in Fig. 9, the hydrogen generation yield was increased due to activation of the catalyst, as increasing from 50 mg to 200 mg the Ni (0) catalyst amount and, then remained almost constant to be hydrogen yield of 98%. These results show that hydrogen generation rate can be determined by controlling the catalyst amount.

### 3.5. Effect of NaOH concentration

Fig. 10 illustrates the hydrogen generation rates with different NaOH concentration, i.e. 1.5 wt%, 5 wt%, and 10 wt%, in 3.2 wt%  $\text{NaBH}_4$  solution with 100 mg of Ni (0) catalyst at 30 °C. As seen in

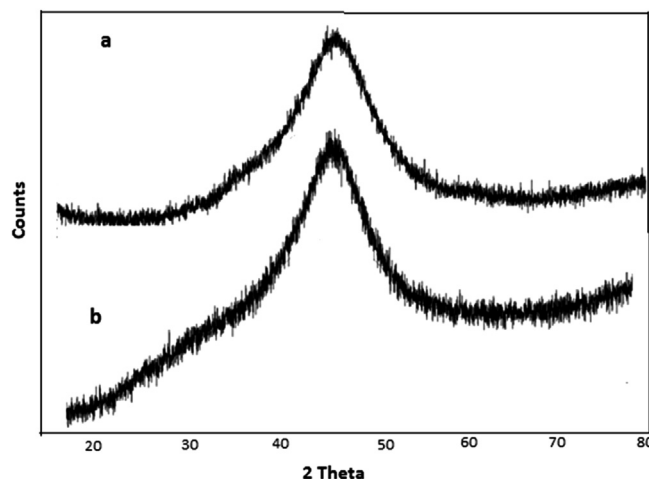


Fig. 5. The comparison of SEM of Ni 2p before (a) and after (b) plasma treatment.

Table 1

The binding energies of Ni 2p, C 1s and O 1s levels and concentrations at.% untreated (a) and treated (b) cold plasma.

Name	Cold plasma treated		Cold plasma untreated	
	Binding energy, eV	Conc. at. %	Binding energy, eV	Conc. at. %
O 1s	531.02	55.62	530.76	52.39
Ni 2p	852.14	20.28	854.82	15.34
C 1s	284.25	24.1	284.05	32.26

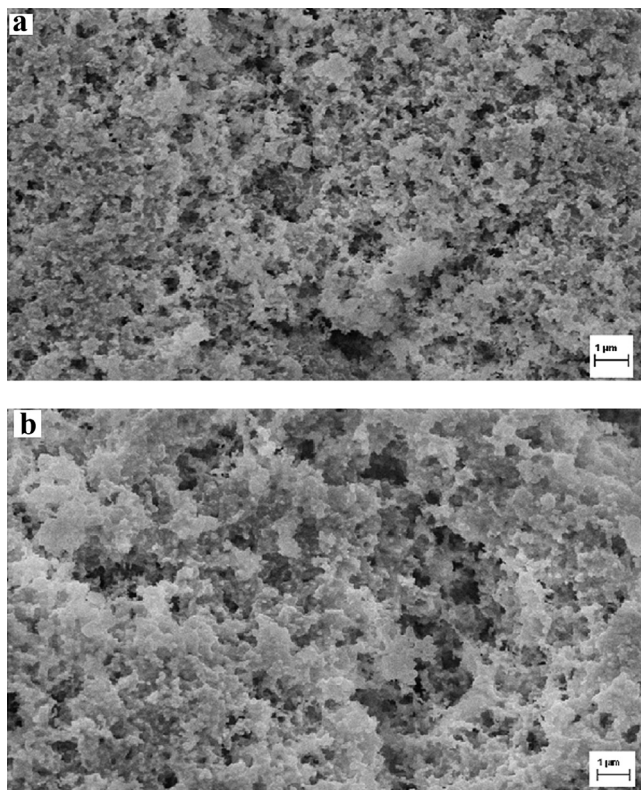


Fig. 6. The comparison of XRD patterns of Ni after (a) and (b) before plasma treatment.

Fig. 10, the hydrogen generation rate was increased with increasing NaOH concentration in NaBH<sub>4</sub> solution with Ni (0) catalyst produced in plasma media. The effect of NaOH concentration on the NaBH<sub>4</sub> hydrolysis rate is similar to Ni<sub>x</sub>B catalysis but completely different from Ru/C catalyzed reaction [20]. As known, the presence of NaOH concentration in NaBH<sub>4</sub> solution is reduced activity of water and viscosity of solution, thus decreasing the available free water to react with NaBH<sub>4</sub> [9]. This explanation cannot account for acceleration effects of NaOH. It is seen that the NaBH<sub>4</sub> hydrolysis on Ni (0) catalyst proceeds in different mechanism, probably involving complicated surface reaction on hydroxide ion with Ni (0) [20].

In the process of NaBH<sub>4</sub> hydrolysis, the accelerating effect of NaOH on Ni (0) catalyzed NaBH<sub>4</sub> hydrolysis may be benefited for the production rate of hydrogen, since H<sub>2</sub>O is stoichiometrically

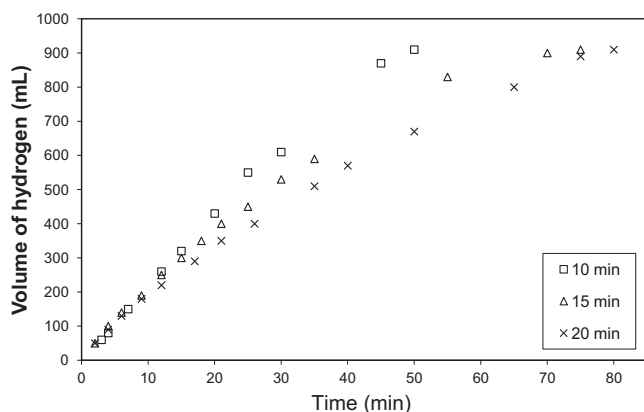


Fig. 7. Effect of plasma applying time.

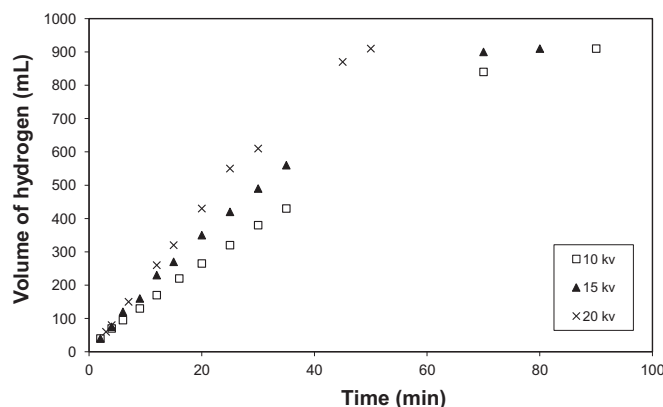


Fig. 8. Effect of plasma applying voltage.

consumed in hydrolysis reaction and give rise to on equivalent increase of NaOH concentration.

### 3.6. Effect of NaBH<sub>4</sub> concentration

The result of hydrogen generation from hydrolysis of NaBH<sub>4</sub> with Ni (0) catalyst in aqueous solution as a function of time for different initial NaBH<sub>4</sub> percentages is presented in Fig. 11. Effect of NaBH<sub>4</sub> concentration on the hydrogen generation rate was measured using  $x$  wt% NaBH<sub>4</sub> ( $x = 3.2, 5, 10$ ), 10 wt% NaOH solutions at 30 °C using 100 mg of Ni (0) catalyst. It is expected that the higher the NaBH<sub>4</sub> concentration in aqueous solution phase, the shorter the hydrolysis time to reach any hydrogen yield percentages. However, as can be seen in Fig. 10, hydrogen yield percentage liberated from NaBH<sub>4</sub> aqueous solution increases with decreasing NaBH<sub>4</sub> percentage in solution. Because of this, the hydrogen yield of 3.2%, 5% and 10% NaBH<sub>4</sub> solution takes the values of 97.20%, 96.45% and 67.33% at the end of 35 min, respectively. A great yield of the hydrogen production at lower weight percentage of NaBH<sub>4</sub> solution is possibly explained by the reduction of solution viscosity as explained in the hydrolysis of NaBH<sub>4</sub> [16]. Besides, the higher the percentage NaBH<sub>4</sub> becomes, the lesser becomes the amount of water.

### 3.7. Effect of temperature

Influence of temperature on hydrogen generation rate in solutions containing 3.2 wt % NaBH<sub>4</sub> and 10 wt % NaOH was investigated at temperatures ranging from 20 °C to 60 °C (Fig. 12). As expected the higher the hydrolysis temperature, the higher the

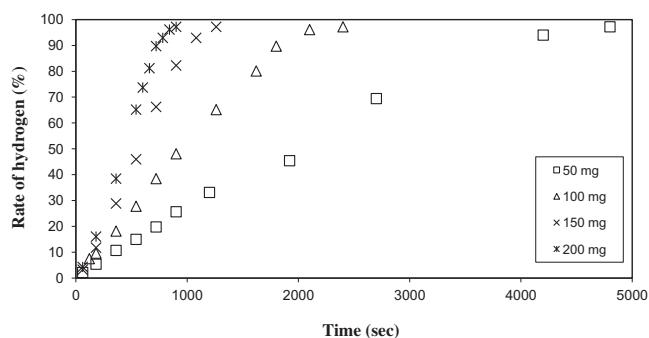
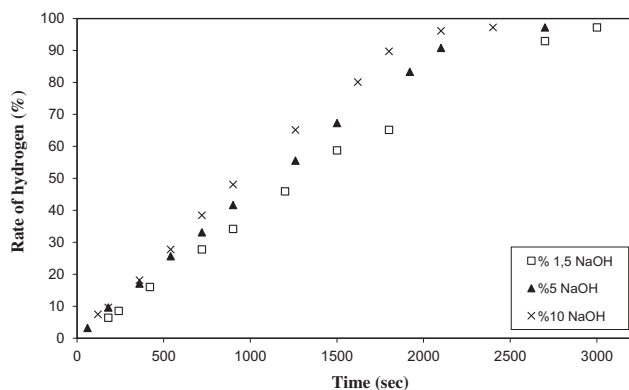


Fig. 9. Effect of Ni (0) catalyst on the hydrogen generation rate measured using 3.2% NaBH<sub>4</sub> + 10 wt% NaOH solutions at 30 °C.



**Fig. 10.** Effect of NaOH concentration on the hydrogen generation rate measured using  $x$  wt% NaOH + 3.2 wt% NaBH<sub>4</sub> solutions ( $x = 1.5, 5, 10$ ) at 30 °C, using 10 mg of Ni (0) catalyst.

hydrogen yield percentage and the shorter the hydrolysis time. Furthermore, the linear relationship between amount of hydrogen generated and reaction time at each temperature studied was observed, demonstrating that such a NaBH<sub>4</sub> hydrolysis reaction is of the zeroth order at temperatures ranging from 20 °C to 60 °C.

For a batch reactor with a volume  $V$ , the reaction rate per unit volume based on zero-order kinetics can be described as:

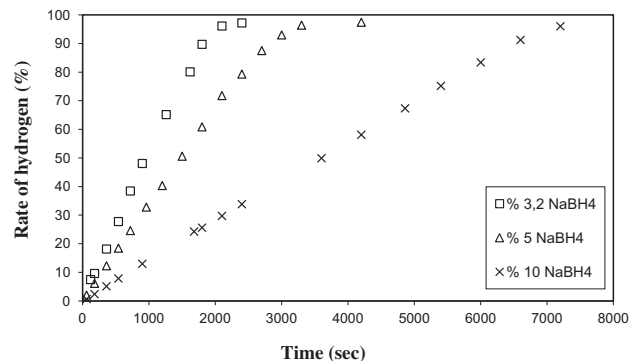
$$\frac{dC_{\text{NaBH}_4}}{dt} = -r_{\text{NaBH}_4} = -k(T) \quad (2)$$

Integrating the differential equation (3), we obtain

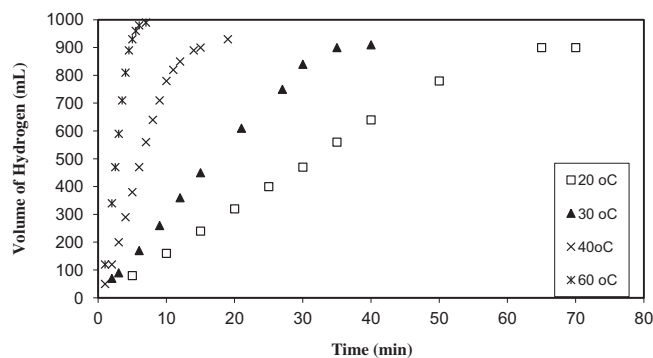
$$C_{\text{NaBH}_4}(t=0) - C_{\text{NaBH}_4}(t=t) = kt \quad (3)$$

where  $C_{\text{NaBH}_4}(t=0)$  is the initial concentration of NaBH<sub>4</sub>,  $C_{\text{NaBH}_4}(t=t)$  is the concentration of NaBH<sub>4</sub> at any time,  $r$  is the rate of reaction and  $k$  is the reaction rate constant based on the solution volume. A plot of  $C_{\text{NaBH}_4}(t=0) - C_{\text{NaBH}_4}(t=t)$  as a function of time should give a straight line passing through the origin and the slope of line can be used to calculate the zero-order rate constant ( $k$ ).

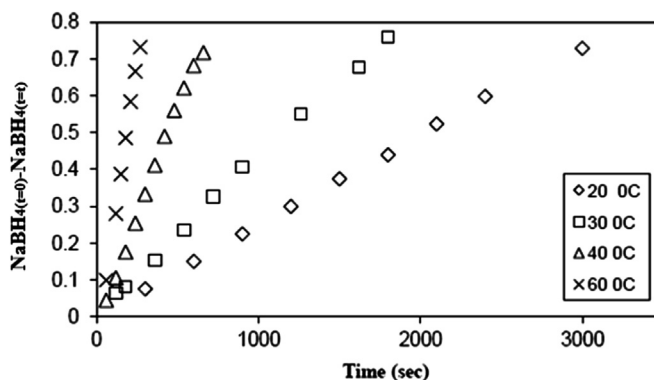
Fig. 13 shows the plot of  $C_{\text{NaBH}_4}(t=0) - C_{\text{NaBH}_4}(t=t)$  versus time for the temperatures of 20, 30, 40 and 60 °C. Here, the maximum hydrogen generation rate was observed from initial condition to 35 min. As can be seen in Fig. 13, at all temperatures where hydrolysis was performed, the zero-order reaction model does fit the curve very well since the plot of  $C_{\text{NaBH}_4}(t=0) - C_{\text{NaBH}_4}(t=t)$  versus time can be represented by linear equation according to regression



**Fig. 11.** Effect of NaBH<sub>4</sub> concentration on the hydrogen generation rate measured using  $x$  wt% NaBH<sub>4</sub> + 10 wt% NaOH solutions ( $x = 3.2, 5, 10$ ) at 30 °C, using 100 mg of Ni (0) catalyst.



**Fig. 12.** Effect of temperature on the hydrogen generation rate measured using 3.2% NaBH<sub>4</sub> + 10 wt% NaOH solutions at 30 °C, using 100 mg of Ni (0) catalyst.

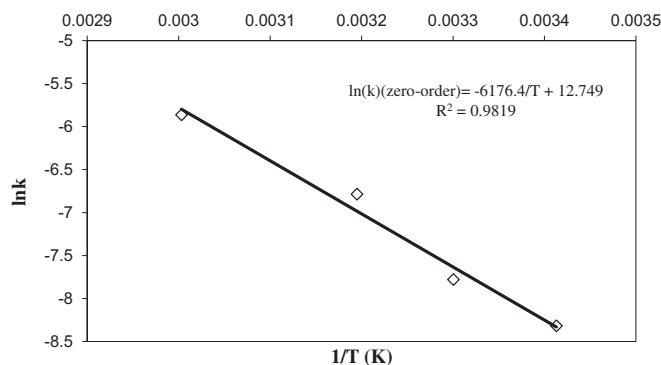


**Fig. 13.** Linear regressions based on zero-order.

with correlation coefficients ( $R^2$ ). As a result, the hydrolysis reaction of NaBH<sub>4</sub> using Ni (0) catalyst prepared with plasma does obey the zero-order reaction model.

In order to find Arrhenius constants (activation energy,  $E$ , and pre-exponential factor,  $A$ ) for zero-order, the plot of  $\ln(k)$  versus  $1/T$  for the temperatures of 20, 30, 40 and 60 °C was obtained and the result is given in Fig. 14. The activation energy and pre-exponential factor of zero-order model can be obtained from slope and intercept of the regression line, being 51.35 kJ mol<sup>-1</sup>,  $3.44 \times 10^5$ . The regression results indicate that the zero-order can describe the hydrogen generation rate with a correlation coefficient of 0.982 at the range of tested temperatures.

Table 2 summarizes the following regression data for zero-order at temperatures range of 20–60 °C, the reaction rate constants

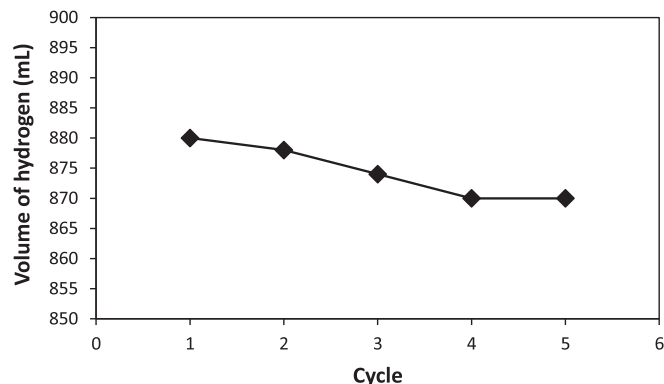


**Fig. 14.** Arrhenius equation according to zero-order.

**Table 2**

Kinetic parameters of hydrolysis of  $\text{NaBH}_4$  with Ni (0) catalyst prepared in the presence of cold plasma for zero-order reaction model.

Zero-order		
$T$	$k$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$R^2$
20	0.000244	0.999
30	0.000418	0.998
40	0.001128	0.989
60	0.00284	0.986



**Fig. 15.** Multi-cycle operations of plasma treated Ni catalyst employing a 3.2%  $\text{NaBH}_4$  + 10 wt% NaOH solutions at 30 °C, using 100 mg of Ni (0) catalyst.

found by the slope of linear regression and the correlation coefficients for regression. The kinetic parameter ( $k$ ) obtained at different temperatures is given in Table 2.

### 3.8. Durability of plasma treated Ni catalyst

Catalyst durability is crucial for sodium borohydride based hydrogen application. In the present study, the plasma treated Ni catalyst prepared under optimized conditions was tested with respect to the durability in the cyclic use. Fig. 15 shows the cycle behavior on hydrogen generation activity for plasma treated Ni catalyst. After each experiment, the used catalyst was separated, washed with deionized water, and dried again. It is evident that the catalyst displayed very similar activity for hydrolysis of  $\text{NaBH}_4$  during the five-cycle operation.

## 4. Conclusions

In this study, the hydrogen production from hydrolysis of  $\text{NaBH}_4$  in the presence of the catalytic properties of Ni (0) prepared with plasma was investigated. The hydrolysis of  $\text{NaBH}_4$  with Ni (0) catalyst in known method and in presence of plasma was investigated depending on  $\text{NaBH}_4$  concentrations in solution, NaOH concentration in solution, temperature. The Ni (0) reduced in the presence of plasma is completed in 35 min time intervals while the Ni (0) produced in known method let to slow hydrogen release and hydrolysis is completed in 80 min time intervals. The yield of hydrogen produced from 3.2%, 5% and 10%  $\text{NaBH}_4$  solution in the presence of plasma is 97.20%, 96.45% and 67.33% at the end of 35 min, respectively. Characteristics of this Ni (0)-based catalyst were carried out by using XRD, BET, SEM and XPS. XPS spectra show that the  $\text{Ni}^{2+}$  species of the catalyst sample are almost completely reduced to Ni (0) during the plasma treatment. XRD spectra after plasma treatment are nearly same as before plasma treatment. The

plasma treated catalyst exhibited significantly higher than surface area ( $23.11 \text{ m}^2 \text{ g}^{-1}$ ) compared to plasma untreated catalyst ( $0.0063 \text{ m}^2 \text{ g}^{-1}$ ). Hydrolysis kinetics of  $\text{NaBH}_4$  in the presence of Ni (0) catalyst was investigated in the presence of plasma at a temperature range of 20–60 °C and zero-order kinetic was applied to the obtained data. The activation energy was found to be  $51.35 \text{ kJ mol}^{-1}$  for zero-order. It can be concluded that the plasma may be used in the hydrogen generation from hydrolysis of  $\text{NaBH}_4$  in the presence of Ni (0) catalyst.

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